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Photoemission study of ferrocenes: insights into the electronic structure of Si-based hybrid materials

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Abstract. We present here the results of synchrotron radiation-excited UV-photoemission investigation and DFT calculations on vinylferrocene (VFC), a redox molecule suitable for applications in molecular electronics. A detailed assignment is discussed of the valence photoelectron spectra (UPS), which provides new data on the electronic structure and offers a partial re-interpretation of previous assignments on VFC based on theoretical and experimental evidences. Furthermore, the present results can allow for a meaningful comparison of photoemission results from the corresponding hybrid obtained by covalently attaching VFC to Si oriented surfaces.

1. Introduction

In the frame of our research line aimed at producing and exploring covalently bound Si-organics hybrid materials for molecular electronics [1] we present here a photoemission and DFT investigation on vinylferrocene (VFC). This work is part of a larger investigation, which we have already carried out on a series of hydrocarbon monosubstituted ferrocenes.

The motivation is twofold: first of all, very little information was thus far available on substituted ferrocenes from photoemission studies. While He(I) and He(II) photoemission valence-band data on ferrocene (Fc), VFC and saturated long-chain substituted ferrocenes are available from previous investigations,[2] the proposed measurements in the valence region are unprecedented. A close comparison of the effect induced on the overall electronic structure of a CH₃-CH₂- moiety with respect to CH₂=CH- and CH≡C- unsaturated groups requires investigating of closely related compounds, with the minimum possible number of further structural variables. On this regard, the three molecules represent a very good choice, since the effect on the geometrical structure of a single C-C lateral group

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basically consists of a very limited deviation from the parallel arrangement of the two cyclopentadienyls reported for unsubstituted ferrocene. Secondly, a detailed information on the free molecule can allow for a meaningful comparison of photoemission results from the corresponding hybrids obtained by covalently attaching ferrocenes to Si oriented surfaces.[1]

2. Experimental and theoretical methods

The experiments were carried out using the angle-resolved photoelectron spectroscopy (ARPES) end station of the gas phase photoemission beam line at the Elettra Synchrotron Light Laboratory (Italy).[3] Vapors of the ferrocene derivative were introduced in the ionization region and kept at constant temperature in the 20-41°C range during the experiment. VFC (Aldrich Purum) was purified by subsequent sublimation cycles. The valence UPS spectrum was found in very good agreement with the He(I) spectrum reported in the literature.[4] The hemispherical electron spectrometer, set at the magic angle and operated in constant pass-energy mode, is a commercial 50 mm mean radius VSW analyzer. The spectrometer is equipped with 1.5 mm entrance and exit slits, thus providing an electron resolution of about 1.5% of the selected pass energy. The valence spectra were calibrated using an Argon leak while vaporizing the solid sample, and recorded at 21.2 eV photon energy with total resolution (photon plus analyzer) of 80 meV (FWHM). Argon spectra were systematically recorded at different photon energies in order to normalize the spectra of the investigated samples with respect to the transmission function of the analyzer, this being dependent on the detected electron kinetic energy. Spectra of ethyl- and ethynyl-ferrocene at different photon energies, not shown here, were also recorded. Vertical ionization energies (IE_v) were determined after peak fitting with asymmetric Gaussian functions.[5] The molecular geometry was optimized and the ionization energies were computed at the DFT level using the hybrid density functional PBE0 [6] (comprising a part of the exact Hartree-Fock exchange functional, and proved very reliable to reproduce the structure and the electronic distribution of organic molecules) and a triple-zeta set of Gaussian basis functions corrected with diffuse and polarization functions. The ionization energy for each electronic state was approximated with the corresponding orbital energy and corrected by the relaxation energy, estimated for the first cation state with the Δ SCF method.

3. Results and Discussion

In VFC the unsaturated substituent group is characterized by the π (C=C) MO. The ionization of this π MO, which is observed in ethylene at 10.51 eV IE_v , [7] can be perturbed quite significantly by the presence of adjacent π MO systems like, e.g., the cyclopentadienyl ring in VFC. The resonance effect of the two π moieties can be rationalized as a through-space interaction between semi-localized π MOs in a Hückel type theory, and depends on the dihedral angle between the molecular planes defined by the atoms of the two π MO conjugated moieties, namely the ethylenic atoms and the cyclopentadienyl-ring. This interaction is the largest in the coplanar geometry.[8] The steric inhibition of resonance is expected to be small because of the little steric hindrance of the vinyl group on rotation from the coplanarity. In fact, a 15° dihedral angle was obtained by DFT molecular geometry optimization. Consequently, large effects on the IE values for some of the outermost MOs should be visible in the PE spectrum. PES investigation of phenylethylene and substituted phenylethylenes has elucidated in detail the effect of the interaction between the ethylene substituent and the aromatic benzene moiety.[8] In phenylethylene, the measured IE values associated with the two interacting π MOs, the π (benzene-based) and π (C=C) MOs, are 8.48 and 10.55 eV.[8,9]

The outer valence PE spectrum obtained in this work is shown in figure 1, while IE_v values, MO characters and ϵ_{MO} are listed in table 1. On going from the ethyl to vinyl substituent in ferrocene derivatives an increase in number of bands in the outer valence region is expected because of the ionization associated with a new π MO with ring-substituent mixed character and mainly located on the C=C ethylene moiety. Six distinct PE bands, here labeled with capital letters, in fact, are discerned in figure 1, as compared with the five observed in ethylferrocene. The low energy band is made of two peaks (A and B) whose IE_v values are 6.88 and 7.27 eV. This band closely resembles the first band in

ferrocene both in IE values and energy separation. This feature is due to the ionization of the e_2' and a_1' ferrocene MOs, with the e_2' energy level not significantly split by the substituent group. The remaining four peaks observed at higher energies are associated with ionization of the five MOs derived from the e_1' and e_1'' ferrocene MOs and the π (C=C) MO.

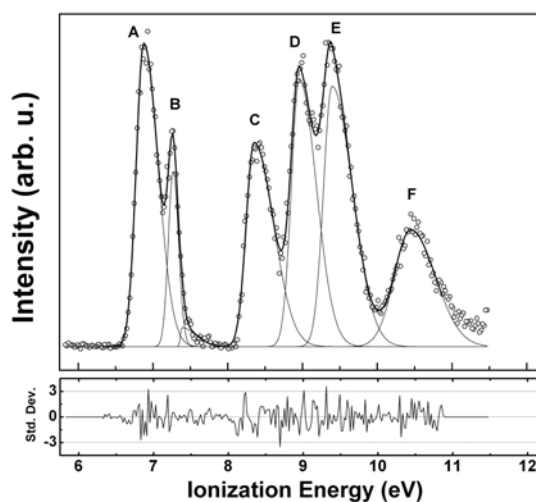


Figure 1. Outer valence PE spectrum of vinylferrocene free molecule recorded at 21.2 eV photon energy (circles) and result of data fitting (lines) with peak labels. Residual in standard deviation units is also shown.

The π conjugation between the cyclopentadienyl ring and the adjacent π (C=C) orbital is quite efficient because resonance is sterically not inhibited due to the quasi-coplanar geometry of the two π systems. The e_1' energy level split is therefore expected to be large, with strong mixing between one of the two e_1' ferrocene MOs and the π (C=C) MO. The PE bands (C and F) accounting for the ionization of the two strongly mixed orbital are observed in figure 1 at 8.35 and 10.45 eV, the latter is referring to the MO mainly located on the ethylenic moiety. The band D at 8.96 eV IE is assigned to the e_1' ferrocene-like MO, which has very modest mixing with the substituent. The remaining peak (E) at 9.39 eV IE is due to the ionization of the e_1'' ferrocene-like MOs. This energy level is not significantly perturbed by the substituent and corresponds to a single PE band in the spectrum. It is worth noting that the 2.10 eV difference in IE value observed between the bands assigned to the ionization of the two π MOs of mixed character (cyclopentadienyl ring (e_1') and the C=C moiety) in VFC is close to the 2.05 and 2.07 eV values measured in phenylethylene,[8,9] where the interaction is between the same ethylenic moiety and the benzene ring. The spectrum in figure 1 can be compared with the He(I) spectrum of VFC published by Matsumura-Inoue *et al.*[4] Both outer valence PE spectra are recorded at the same photon energy, 21.2 eV.

Table 1. Vertical ionization energies (IE_v), calculated MO characters, and ε_{MO} energies for vinylferrocene. MO labels are derived from ferrocene, for identification.

Band label	IE_v (eV)	MO main character	$-\varepsilon_{MO}$ (eV)
A	6.88	e_2'	5.87, 5.94
B	7.27	a_1'	6.71
C	8.35	$e_1' + \pi$ (C=C)	6.55
D	8.96	e_1'	7.20
E	9.39	e_1''	7.54, 7.69
F	10.45	π (C=C)	8.60

Although differently polarized photon sources have been used, the two spectra of VFC can be compared consistently since the present data are obtained at the magic angle with respect to the polarization direction of the linearly polarized synchrotron radiation. This setup, in fact, allows the PE measurements to be independent from anisotropy in the photoelectron angular distribution and thus permits a direct comparison with spectra excited by unpolarized He(I) radiation. The five outermost PE bands in figure 1 are in good agreement with the He(I) spectrum with respect to the energy pattern, relative intensities, and band profiles. However, the sixth band (F), measured in the present work at 10.45 eV IE, is not included in the IE range of the published He(I) spectrum. This band, which is important for elucidating the valence electronic structure of the ferrocene derivative, is assigned by us to the ionization of a vinyl(C=C)/ring mixed π MO, which is mainly located on the vinyl moiety. The corresponding partner in the interaction (π MO mixing) is the MO with ring(e_1')/vinyl(C=C) mixed character and mainly located on the cyclopentadienyl ring, whose ionization has been associated with the band C at 8.35 eV IE. The assignment of this band in the He(I) spectrum is different, and the structure has been associated with the ionization of an electron in a vinyl group.[4] These authors support the assignment by citing the similar case of vinyl group in phenylethylene.[8] According to the study of the valence PE spectrum of phenylethylene by Rabalais *et al.*,[9] however, the ionization of a π electron from the vinyl group in phenylethylene must be ascribed instead to the band at 10.55 eV IE, this value being near the one observed in ethylene (10.51 eV). Moreover, the assignment by Rabalais *et al.* is in accord with the correlation diagram of figure 4(a) reported in reference 8. Therefore, the correct assignment of the ionization of the π -vinyl MO in phenylethylene supports the assignment of the valence PE spectra of the VFC proposed in the present work. It should be mentioned that the previous PE study of VFC [4] did not benefit from a theoretical investigation. The present experimental assignment is corroborated by the MO energies and MO compositions obtained theoretically for VFC in this work.

Acknowledgments

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